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LAWS GOVERNING THE OCCURENCE OF RARE EARTH ELEMENTS

by

Yu. A. Balashov

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LAWS GOVERNING THE OCCURRENCE OF RARE EARTH ELEMENTS IN THE EARTH'S CRUST[1]

Yu. A. Balashov

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ABSTRACT

Correlation ratios of rare earth elements were established and a systematic study was made of rare earth elements in rocks of the earth's crust.

Maximum variations in rare earth elements were observed in alkaline rocks and granites. On the average, massifs formed by alkaline rocks and granitoids were distinguished by a strong prevalence of the cerium group as compared with ultrabasic and basic rocks.

All rocks of the earth's crust (including sedimentary and metamorphic) are distinguished by a higher content of rare earth elements (with relative concentrations of the cerium group) as compared with the silicate phase of chondrites assumed to be analogous to the matter in the mantle.

The mantle is probably connected with dissemination chiefly of the yttrium group of rare earth elements in abyssal differentiates of the mantle (dunites) due to isomorphic dispersion of rare earth elements in Fe- and Mg silicates.

The rare earth elements which occupy an isolated position in the periodic table due to the specific nature of their electron shell structure reflect the most important properties of this table in miniature: an increase in basicity with increased ionic radius of the element (in a vertical direction in the table) and periodicity in changes in their chemical and physical properties (in a horizontal direction).

In addition, the similarity of the chemical properties of rare earth elements which permit one to regard them in the first approximation as one element is caused by common migration routes of the rare earth elements and their joint occurrence in different natural objects.

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1 Geokhimiya, No. 2, pages 99-114, 1963

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In spite of the interest in rare earth elements, their study was of a somewhat one-sided nature for a long time, being associated essentially with rare earth minerals. Information on the occurrence of rare earth elements in the rocks of the earth's crust was limited and fragmental, and this produced very contradictory ideas concerning these elements.

Since 1959 the author has been conducting research on the general laws governing the occurrence of rare earth elements in the rocks of the earth's crust which permit one to explain the variety and the specifics of the occurrence of rare earth elements in different types of rock; to establish correlation ratios of rare earth elements in rocks and basic trends in the magmatic evolution of rare earth elements during the formation of individual massifs; and also to note routes of separation of rare earth elements in the upper parts of the earth's mantle during the formation of the earth's crust.

Correlation ratios of rare earth elements in rocks are examined in this article and general information is presented on the distribution of rare earth elements in different rocks and in the earth's crust as a whole.[1]

Contemporary Ideas on the Prevalence of Rare Earth Elements in the Earth's Crust

Although more than 160 years have passed since rare earth elements were discovered, detailed familiarity with the literature on the geochemistry of these elements reveals that even now there is no agreement on the nature of the distribution of rare earth elements in the rocks of the earth's crust.

Present ideas on this problem can be divided into three groups which reflect to a certain extent the evolution of ideas on the basic problems of rare earth element geochemistry in the last four decades.

1. In works by Rankama and Sahama (1950, Ref. 58), Goldschmidt (1954, Ref. 51), Suess and Urey (1956, Ref. 64), and Taylor (1960, Ref. 66), it is pointed out that rare earth elements comprise a large unified group of chemical elements that have not undergone serious fractionation in the earth.

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[1] Information on the occurrence of rare earth elements in the magmatic process is generalized in another article by the author (in a collection of articles dedicated to the 100th anniversary of the birth of V. I. Vernadskiy).

These views on the relative constancy of the composition of rare earth elements in the earth's crust were developed in the 1930's, (Hevesy, 1929, Ref. 40; Goldschmidt, 1933, 1937, Refs. 49, 50) as generalized data on the geochemistry of rare earth elements obtained from 1908 to 1935 (Eberhard, 1908, Ref. 44; Goldschmidt and Thomassen, 1924, Ref. 45; Goldschmidt, Ulrich, and Barth, 1925, Ref. 46; Goldschmidt, 1926, 1930, Refs. 47, 48; Russell, 1929, Ref. 59; Minami, 1935, Ref. 54; Noddack, 1935, Ref. 57, and others). /100

2. The opposite opinion on differentiation of rare earth elements in rocks of the earth's crust was developed in a number of works by other investigators (Borodin, 1960, Ref. 12; Balashov and Turanskaya, 1960, 1962, Refs. 2, 3, 8; Zlobin and Balashov, 1961, Ref. 28; A. P. Vinogradov, 1961, 1962, Refs. 21, 22, 23; Vaynshteyn, Pavlenko, Turanskaya, Yulova, 1961, Ref. 16; Shvey, 1962, Ref. 41; Balashov, 1962, Ref. 7; Taylor, 1962, Ref. 67). However, in their arguments, there are definite differences in the ideas on the occurrence of rare earth elements in the principal types of igneous rocks.

a) Thus, L. S. Borodin and I. V. Shvey base their opinions chiefly on data from analysis of accessory minerals.

In fact, a great deal of factual material has been accumulated recently on rare earth elements in minerals, and most of it in the last ten years. Correlation ratios of rare earth elements in minerals have been established as the result of work done by Murata and co-workers (1953-1957, Refs. 55, 56; Vaynshteyn, Tugarinova, and Turanskaya, 1955, 1956, Refs. 13, 14, 15; Semenov and Barinskiy, 1958, Refs. 32, 33), and many others, and it has been shown that the composition of rare earth elements in the same mineral species varies in accordance with the genesis of the mineral (confirmation of Vernadskiy's proposition, 1929, Ref. 17).

All this research permits one to speak with considerable confidence on the possibility of different composition of rare earth elements in rocks, but does not by any means lead to correct conclusions on the trend of changes at all times.

Although Borodin (1960) stated that the cerium group of rare earth elements accumlates in alkaline rocks while the yttrium group accumulates in acid rocks, Shvey (1962) believes that the light lanthanides occur in basic and alkaline rocks and to a lesser degree in granites; on the other hand, yttrium and its rare earth analogs (Ref. 41) are more characteristic of alkaline granites.

A comparison shows that these ideas are contradictory, and they are not original since they add details to propositions advanced earlier by Fersman (1939, Ref. 38) and Haberlandt (1947, Ref. 39), and, what is most important, they do not correspond to direct determinations of rare earth elements in basic and acid rocks. Thus, Sahama (1945, Ref. 31) utilized X-ray spectral analysis to show that gabbro and dolerites are relatively rich in the yttrium group as compared with the granites of Southern Finnish Lapland.

This sort of divergence between theory and factual data is caused by the separation in nature of rare earth elements by accessory minerals (with a predominance of ΣCe in some and concentrations of ΣY in others (Refs. 2,3,24), thus it is difficult to judge the composition of rare earth elements in rock without a detailed mineralogical balance. Moreover, there are no grounds for believing that rare earth elements are concentrated primarily in accessory minerals in all rocks. In fact, an investigation of monazite-containing Kirovograd granite showed that about 40 percent of the rare earth elements were dispersed in rock-forming minerals (Gavrilova and Turanskaya, 1958, Ref. 24); 25 to 65 percent of all the yttrium in the rock was concentrated in hornblendes of the granitoids of the Southern California batholith (Sen, Nockolds, and Allen, 1959, Ref. 62).

Judging the rare earth element content by accessory minerals can turn out to be erroneous. For example, according to A. S. Pavlenko's data, a comparison of the composition of rare earth elements in monazite-containing granite from Ukrainia and in orthite-containing granite from the Agash Massif (Eastern Tuva Autonomous Oblast'), shows that cerium rare earth elements ($\Sigma Ce/\Sigma Y = 4.7$, Table 4) are dominant in the first and relative richness of the yttrium group ($\Sigma Ce/\Sigma Y = 1.2$, Table 1) is observed /101
in the second. The composition of rare earth elements in the principal accessory concentrators of rare earth elements--monazite and orthite--from these rocks is marked by a reverse ratio. The lighter lanthanides of the cerium group predominate more sharply in orthite (Ce/Nd = 3.1) than in monazite (Ce/Nd = 2.6).

b) The second group of investigators who defend the idea of differentiation of rare earth elements in rocks of the earth's crust depend on direct analyses of rare earth elements in rocks.

Up to 1960 information on rare earth elements in rocks was limited to 35-40 X-ray spectral determinations, chiefly of shales and granites (Minami, 1935, Ref. 54; Sahama and Yahatalo, 1939, Ref. 60; Sahama, 1945, Ref. 61; Vaynshteyn, Tugarinov, and Turanskaya, 1956, Ref. 15; Gavrilova, Turanskaya, 1958, Ref. 24) and also semi-quantitative spectral analyses (Van Tongeren, 1938, Ref. 65; Nockolds and Allen, 1958, Ref. 30; Landergren, 1936, Ref. 52, and others).

Improvements in chemical methods for concentrating rare earth elements from rocks for X-ray spectral analysis (Balashov, 1961, Ref. 5; Balashov, Turanskaya, Ref. 6) and the introduction of activation analysis into the practice of geochemical investigations (Schmitt and others, 1960, Ref. 5) ensured a sharp expansion of work on determining rare earth elements in rocks and meteorites in the last two years.

Here we must note the appearance of new data on the composition of rare earth elements in the silicate phase of chondrites (Schmitt and others, 1960, Ref. 63) and the first figures on Dy and Eu in dunites (A. P. Vinogradov, 1961, Ref. 21).

An analysis of factual material on the prevalence of rare earth elements in igneous rocks, taking account of new determinations of rare earth elements in meteorites and in dunite, permit one to note basic tendencies in the distribution of rare earth elements in the formation of the earth's crust. A. P. Vinogradov (Refs. 21, 22) pointed out for the first time a directed variation in the composition of rare earth elements ranging from meteorites ($\Sigma Ce/\Sigma Y = 1.3$) to basalts ($\Sigma Ce/\Sigma Y = 2.0$) and granites ($\Sigma Ce/\Sigma Y = 3.5$) toward relative accumulation of the cerium group in acid rocks.[1]

Using Eu and Dy as examples, A. P. Vinogradov (1961) also noted that the rare earth element content increased from dunites to meteorites and from the latter to basalts (and granites) which, with data on many other elements, is in good agreement with the mechanism of the melting of the earth's crust from the material of the mantle which was proposed by A. P. Vinogradov (Refs. 20, 21).

However, Taylor arrived at a different conclusion in his latest article on the prevalence of rare earth elements in the earth's crust and in meteorites (1962, Ref. 67) where he assumed that the composition of rare earth elements in meteorites and in basalts is identical while concentration of the cerium group is observed in granites, even though his reasoning is based on comparison of the very same data on rare earth elements in the silicate phase of chondrites (Schmitt and others, Ref. 63) and in gabbro and dolerites (Sahama, Refs. 31, 60).

In the period 1960 to 1962 the first information was published on the behavior of rare earth elements in comagmatic series of alkaline rocks (Refs. 2, 3, 7, 28) and the distribution of rare earth elements in different petrochemical types of rocks belonging to a genetically like differentiated granitoid intrusive complex (Ref. 16). These works cast light for the first time on some very important features of the geochemistry of rare earth elements in the magmatic process:

a) It was shown that the composition and content of rare earth elements can vary considerably even in a single petrographic group

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[1]All ratios $\Sigma Ce/\Sigma Y$ without Y.

of rocks (nepheline syenites, Refs. 7, 16; syenites, Refs. 28, 16; and granites, Ref. 16).

b) The evolution of the composition of rare earth elements differs according to intrusive phases of comagmatic alkaline series--both light lanthanides (Ref. 28) and heavy lanthanides (Ref. 7) can accumulate by the end of the magmatic process.

c) The variation in the composition of rare earth elements by intrusive phases made up of alkaline rocks (the Lovozero Massif and the Sandyk Massif, Ref. 7) is correlated with the evolution of the chemical composition of the phases (with changes in the a and c petrochemical /102

parameters[1]) within individual massifs. This connection has not been established for the more extensive series of differentiation of granitoid magma in which the composition of rare earth elements in the rocks depends on the conditions of alkalinity during crystallization of the rocks (Ref. 16).

Finally, the appearance in 1957 to 1962 of new data on rare earth element content in different types of rocks (including spectral determinations of certain rare earth elements (Ref. 42) permitted an important revision of the rare earth element content in different types of rocks and in the earth's crust (A. P. Vinogradov, 1962, Ref. 23). As compared with earlier generalizations (A. P. Vinogradov, 1950, 1956; Refs. 18, 19) the average contents of rare earth elements in stony meteorites were decreased while they were increased in the principal acid rocks and on the whole in the earth's crust.

Variations in the Composition and Content of Rare Earth Elements in the Rocks of the Earth's Crust

Systematic investigations of rare earth elements in alkaline intrusions, then in granitoid and other rocks which were started in 1959 have permitted the accumulation of a considerable amount of factual material on the distribution of rare earth elements in rocks.

The composition of rare earth elements was analyzed with the participation and under the guidance of Turanskaya by means of an X-ray spectral method (Refs. 15, 37), with an accuracy of 5 to 8 percent for individual elements. The total rare earth element content was determined by a photocolorimetric method (Ref. 27) (when necessary, with improvements (Ref. 4)) which had accuracy of 6 to 20 percent.

[1]The petrochemical parameters of A. N. Zavaritskiy.

The $\Sigma Ce/\Sigma Y$ ratio where ΣCe includes La - Eu and ΣY includes Gd - Lu + Y (Y is also included in ΣTR_2O_3) was employed for comparing the composition of rare earth elements in rocks.

The summary (Table 1) contains known analyses of rare earth elements in igneous, sedimentary, and metamorphic rocks which characterize the established limits of fluctuations in the composition and content of rare earth elements in individual types of rocks. The table also includes data on the average content of rare earth elements in the earth's crust (Ref. 23) and calculated average composition of rare earth elements in individual massifs.

A diagram (page 8) of variations in the composition of rare earth elements was constructed in accordance with the data in the table which shows significant changes in the prevalence of rare earth elements in different types of rocks.

The factual material cited here permits one to draw certain conclusions on the distribution of rare earth elements in rocks.

1. Fluctuations in the composition and content of rare earth elements decrease as we go from alkaline rocks and granites to basic and ultrabasic rocks:

	$\Sigma Ce/\Sigma Y$	TR_2O_3,%
Nepheline syenites, syenites, alkaline ultrabasic and basic rocks	1.2-30-(48)	$1.6\text{-}60\cdot10^{-2}$ and higher
Granites	1.2-12	$2.7\text{-}15\cdot10^{-2}$
Sedimentary and metamorphic rocks	0.2-4.6	$0.3\text{-}8\cdot10^{-2}$
Basic and ultrabasic rocks (without dunites)	1.0-1.2	$0.09\text{-}0.3\cdot10^{-2}$

It is necessary to note, however, that at present very little data are available on ultrabasic, basic, and sedimentary rocks and that systematic investigations of these rocks for rare earth elements are lacking.

2. In spite of considerable fluctuations in the composition of rare earth elements in nepheline syenites, syenites, and granites, the average composition of rare earth elements in massifs made up of these rocks is marked by a sharp predominance of the cerium group ($\Sigma Ce/\Sigma Y$ = 4-5). /103

Table 1. The Content of Rare Earth Elements in the Rocks of the Earth's Crust and in Meteorites (in Per Cent)

Rock	Area	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu	Y	$\frac{\Sigma Ce}{\Sigma Y}$	$\frac{Ce}{Nd}$	TR_2O_3	Author
I. Meteorites (silicate phase of chondrites)																				
Meteorite	—	2.0×10^{-4}	2.3×10^{-4}	9.7×10^{-5}	3.4×10^{-4}	1.2×10^{-4}	3.0×10^{-5}	1.8×10^{-4}	5.8×10^{-5}	2.3×10^{-4}	6.6×10^{-5}	1.9×10^{-4}	3.4×10^{-5}	1.8×10^{-4}	6.0×10^{-5}	6.1×10^{-4}	0.4	0.68	2.4×10^{-3}	[57][1]
"	—	3.3×10^{-5}	5.5×10^{-5}	1.2×10^{-5}	6.5×10^{-5}	2.4×10^{-5}	8.7×10^{-6}	3.4×10^{-5}	4.9×10^{-6}	3.9×10^{-5}	8.2×10^{-6}	2.2×10^{-5}	4.3×10^{-6}	1.9×10^{-5}	3.8×10^{-6}	—	(0.55)	0.85	(6.6×10^{-4})	[63]
"	—	3.2×10^{-5}	4.8×10^{-5}	1.2×10^{-5}	6.1×10^{-5}	2.0×10^{-5}	8.0×10^{-6}	3.4×10^{-5}	5.3×10^{-6}	3.4×10^{-5}	6.8×10^{-6}	2.0×10^{-5}	3.3×10^{-6}	1.9×10^{-5}	3.3×10^{-6}	—	(0.55)	0.79	(6.1×10^{-4})	[63]
II. Ultrabasic, basic, and intermediate rocks																				
Dunite	China, Tyan-Shan'	—	—	—	—	—	1.0×10^{-4}	—	—	5.0×10^{-6}	—	—	—	—	—	—	(0.4)	(≈ 1)	(8×10^{-5})	[21]
Pyroxenite	Kola Peninsula, Monche-Tundra	6.5×10^{-5}	1.4×10^{-4}	2.2×10^{-5}	1.1×10^{-4}	3.4×10^{-5}	—	4.4×10^{-5}	—	4.0×10^{-5}	—	3.2×10^{-5}	—	2.8×10^{-5}	—	2.1×10^{-4}	1.0	1.3	9.0×10^{-4}	Yu. A. Balashov
"	Same	1.9×10^{-4}	5.1×10^{-4}	—	3.8×10^{-4}	—	—	—	—	—	—	—	—	—	—	—	(1.0)	1.35	2.6×10^{-3}	"
Peridotite	Urals, Marun-Keu	1.8×10^{-4}	3.3×10^{-4}	6.0×10^{-5}	2.4×10^{-4}	8.8×10^{-5}	—	9.0×10^{-5}	1.9×10^{-5}	9.5×10^{-5}	2.4×10^{-5}	4.7×10^{-5}	—	5.7×10^{-5}	—	4.8×10^{-4}	1.1	1.4	2.0×10^{-3}	[8]
Gabbro and dolerites	Finland, Southern Lapland	1.7×10^{-4}	3.4×10^{-4}	8.5×10^{-5}	4.3×10^{-4}	8.6×10^{-5}	—	1.7×10^{-4}	—	8.7×10^{-5}	—	8.7×10^{-5}	—	8.8×10^{-5}	—	4.7×10^{-4}	1.2	0.8	2.4×10^{-3}	[31]
Diabase	Standart W-1	3.0×10^{-3}	7.0×10^{-3}	—	5.0×10^{-3}	—	—	—	—	—	—	—	—	2.0×10^{-3}	—	3.0×10^{-3}	(1.5)	1.4	—	[42]
Gabbro-diorites and diorites	Tyan-Shan', Susamyr	4.5×10^{-3}	9.0×10^{-3}	1.3×10^{-3}	4.7×10^{-3}	1.2×10^{-3}	—	1.1×10^{-3}	3.1×10^{-4}	1.1×10^{-3}	3.8×10^{-4}	5.7×10^{-4}	—	6.5×10^{-4}	—	6.4×10^{-3}	1.9	1.9	3.8×10^{-2}	Yu. A. Balashov
III. Granites and granodiorites																				
Granite	Western Tuva Oblast', Agash Massif	2.2×10^{-3}	4.5×10^{-3}	8.7×10^{-4}	3.6×10^{-3}	9.0×10^{-4}	—	9.7×10^{-4}	—	7.9×10^{-4}	1.1×10^{-4}	5.4×10^{-4}	—	5.5×10^{-4}	—	7.2×10^{-3}	1.2	1.3	2.7×10^{-2}	Yu. A. Balashov
"	Western Tuva Oblast', Nizhne-Kadrausskiy Region	5.3×10^{-3}	1.0×10^{-2}	1.2×10^{-3}	4.8×10^{-3}	1.1×10^{-3}	—	1.1×10^{-3}	4.3×10^{-4}	1.2×10^{-3}	3.0×10^{-4}	8.8×10^{-4}	—	1.0×10^{-3}	—	8.8×10^{-3}	1.7	2.0	4.2×10^{-2}	"
Leucocratic granites	Tyan-Shan', Susamyr	6.3×10^{-3}	1.2×10^{-2}	1.4×10^{-3}	5.3×10^{-3}	1.3×10^{-3}	—	1.2×10^{-3}	3.2×10^{-4}	1.1×10^{-3}	4.2×10^{-4}	7.4×10^{-4}	—	7.4×10^{-4}	—	7.5×10^{-3}	2.0	2.3	4.4×10^{-2}	"
Granite	Finland, Obnes	2.6×10^{-2}	4.3×10^{-2}	6.0×10^{-3}	1.7×10^{-2}	5.2×10^{-3}	8.6×10^{-4}	6.9×10^{-3}	8.7×10^{-4}	2.6×10^{-3}	8.7×10^{-4}	2.6×10^{-3}	8.0×10^{-4}	1.7×10^{-3}	8.8×10^{-4}	1.6×10^{-2}	2.8	2.5	1.5×10^{-1}	[60]
Granite (No 1052 [15, 24])	Ukrainia, Kirovograd	6.6×10^{-3}	1.5×10^{-2}	1.9×10^{-3}	7.6×10^{-3}	1.5×10^{-3}	—	8.6×10^{-4}	2.7×10^{-4}	8.4×10^{-4}	—	3.8×10^{-4}	—	3.6×10^{-4}	—	3.8×10^{-3}	4.7	2.0	4.6×10^{-2}	Yu. A. Balashov
Rapakivi granite (No 1055 [15])	Ukrainia, Ustinovskiy	9.0×10^{-3}	1.9×10^{-2}	2.3×10^{-3}	9.5×10^{-3}	1.8×10^{-3}	—	1.2×10^{-3}	—	9.5×10^{-4}	—	2.0×10^{-4}	—	1.9×10^{-4}	—	2.0×10^{-3}	5.8	2.0	5.5×10^{-2}	Same
Granodiorites	Tyan-Shan', Susamyr	9.2×10^{-3}	1.7×10^{-2}	2.0×10^{-3}	6.6×10^{-3}	1.1×10^{-3}	—	7.0×10^{-4}	—	6.7×10^{-4}	—	3.4×10^{-4}	—	3.2×10^{-4}	—	3.6×10^{-3}	5.8	2.6	4.9×10^{-2}	Same
Granite	Western Tuva Oblast', Radyrosskiy	1.3×10^{-2}	2.1×10^{-2}	1.9×10^{-3}	5.8×10^{-3}	9.3×10^{-4}	—	6.4×10^{-4}	—	4.6×10^{-4}	—	2.3×10^{-4}	—	1.7×10^{-4}	—	2.9×10^{-3}	9.0	3.7	5.5×10^{-2}	Same
Alaskite granites	Tyan-Shan', Kzyl-Ompul	8.0×10^{-3}	1.2×10^{-2}	1.2×10^{-3}	3.3×10^{-3}	3.3×10^{-4}	—	2.6×10^{-4}	—	1.6×10^{-4}	—	1.0×10^{-4}	—	1.0×10^{-4}	—	1.0×10^{-3}	12.0	3.6	3.0×10^{-2}	Same
IV. Alkaline ultrabasic and basic rocks																				
Alkaline ultrabasic rocks	Kola Peninsula	3.6×10^{-2}	7.5×10^{-2}	7.7×10^{-3}	2.9×10^{-2}	3.0×10^{-3}	3.8×10^{-3}	1.6×10^{-3}	9.4×10^{-5}	3.9×10^{-4}	3.1×10^{-5}	6.3×10^{-5}	7.8×10^{-6}	1.2×10^{-4}	3.1×10^{-5}	2.0×10^{-3}	(35)	2.6	1.6×10^{-1}	[29]**
Alkaline gabbroids	Tyan-Shan', Sandyk	2.7×10^{-3}	6.0×10^{-3}	7.0×10^{-4}	3.2×10^{-3}	7.0×10^{-4}	—	7.0×10^{-4}	—	5.0×10^{-4}	—	3.0×10^{-4}	—	5.0×10^{-4}	—	3.5×10^{-3}	2.9	1.9	2.2×10^{-2}	[28]
V. Syenites																				
Syenito-diorite	Georgian SSR, Adzhariya, Merisi	4.5×10^{-3}	1.1×10^{-2}	1.6×10^{-3}	6.4×10^{-3}	1.4×10^{-3}	—	1.7×10^{-3}	—	1.3×10^{-3}	—	1.1×10^{-3}	—	—	—	—	1.6	1.6	4.9×10^{-2}	Yu. A. Balashov
Alkaline porphyries	Armeniya, Pambakskiy	4.9×10^{-2}	1.1×10^{-1}	1.7×10^{-2}	7.6×10^{-2}	1.8×10^{-2}	—	1.3×10^{-2}	—	1.5×10^{-2}	—	6.1×10^{-3}	—	—	—	6.3×10^{-2}	2.3	1.4	4.4×10^{-1}	Same
Grano-syenites	Tyan-Shan', Kzyl-Ompul	4.1×10^{-3}	8.8×10^{-3}	1.3×10^{-3}	5.2×10^{-3}	1.3×10^{-3}	—	1.1×10^{-3}	—	9.0×10^{-4}	—	5.2×10^{-4}	—	5.1×10^{-4}	—	5.0×10^{-3}	2.4	1.7	3.5×10^{-2}	Same
Syenites	Same	4.7×10^{-3}	9.4×10^{-3}	1.2×10^{-3}	4.5×10^{-3}	1.0×10^{-3}	—	7.7×10^{-4}	—	8.5×10^{-4}	—	4.0×10^{-4}	—	3.6×10^{-4}	—	4.0×10^{-3}	3.0	2.1	3.3×10^{-2}	Same
Alkaline syenites	Tyan-Shan', Sandyk	9.2×10^{-3}	1.8×10^{-2}	2.0×10^{-3}	7.7×10^{-3}	1.5×10^{-3}	—	9.0×10^{-4}	—	6.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}	—	—	—	4.6×10^{-3}	4.9	2.3	5.3×10^{-2}	[28]
Granosyenite	Western Tuva Oblast', Dugdinskiy	1.1×10^{-2}	1.7×10^{-2}	1.8×10^{-3}	6.0×10^{-3}	1.2×10^{-3}	—	8.4×10^{-4}	—	5.4×10^{-4}	—	3.0×10^{-4}	—	—	—	3.0×10^{-3}	6.9	2.9	7.0×10^{-2}	"
Biotite syenite	Urals, Bishnevya Gory	1.1×10^{-2}	1.7×10^{-2}	2.0×10^{-3}	5.0×10^{-3}	1.0×10^{-3}	—	—	—	—	—	—	—	—	—	—	10	3.4	4.5×10^{-2}	Yu. A. Balashov

Table 1. Continued.

Rock	Area	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu	Y	ΣCe/ΣY	Ce/Nd	TR_2O_3	Author
VI. Nepheline syenites																				
Eudialyte lujaurite	Kola Peninsula, Lovozero	2.7×10^{-2}	5.1×10^{-2}	6.9×10^{-3}	3.0×10^{-2}	9.0×10^{-3}	—	$9.0\times10^{-[illegible]}$	2.4×10^{-3}	9.9×10^{-3}	3.0×10^{-3}	5.7×10^{-3}	—	6.0×10^{-3}	—	6.0×10^{-2}	1.4	1.7	2.6×10^{-1}	[3]
Red kakortokite	Southern Greenland, Ilimaussak	7.1×10^{-2}	1.4×10^{-1}	2.0×10^{-2}	7.9×10^{-2}	2.1×10^{-2}	—	$1.7\times10^{-[illegible]}$	3.2×10^{-3}	1.9×10^{-2}	4.7×10^{-2}	1.1×10^{-2}	—	1.3×10^{-2}	—	1.1×10^{-1}	1.8	1.7	5.9×10^{-1}	Yu. A. Balashov
Aegirine lujaurite	Same	7.8×10^{-2}	1.7×10^{-1}	2.1×10^{-2}	7.8×10^{-2}	1.4×10^{-2}	—	$1.6\times10^{-[illegible]}$	3.1×10^{-3}	1.3×10^{-2}	—	7.8×10^{-3}	—	7.0×10^{-3}	—	7.5×10^{-2}	2.7	2.2	5.8×10^{-1}	Same
Nepheline syenite	Alayskiy Range, Turpi	5.6×10^{-3}	1.1×10^{-2}	1.4×10^{-3}	5.1×10^{-3}	1.2×10^{-3}	—	$8.7\times10^{-[illegible]}$	2.0×10^{-4}	9.2×10^{-4}	2.5×10^{-4}	3.6×10^{-4}	—	—	—	3.6×10^{-3}	3.7	2.1	3.6×10^{-2}	Same
Massive khibinite	Kola Peninsula, Khibiny Gory	1.2×10^{-2}	2.2×10^{-2}	2.8×10^{-3}	1.0×10^{-2}	1.6×10^{-3}	—	$1.2\times10^{-[illegible]}$	3.0×10^{-4}	1.0×10^{-3}	3.1×10^{-4}	4.1×10^{-4}	—	5.2×10^{-4}	—	6.2×10^{-3}	5.2	2.2	7.0×10^{-2}	Same
Miaskite	Urals, Vishnevye Gory	3.6×10^{-3}	5.7×10^{-3}	5.7×10^{-4}	1.9×10^{-3}	3.2×10^{-4}	—	$2.3\times10^{-[illegible]}$	—	2.2×10^{-4}	—	1.1×10^{-4}	—	—	—	—	6.5	3.0	1.6×10^{-2}	Same
Melanocratic lujaurite	Kola Peninsula, Lovozero	1.3×10^{-1}	2.4×10^{-1}	2.2×10^{-2}	6.4×10^{-2}	7.0×10^{-3}	—	3.8×10^{-1}	—	1.3×10^{-3}	—	—	—	—	—	—	(48)	3.7	5.6×10^{-1}	[2]
VII. Veins in rocks, pegmatites, metasomatites																				
Hydrothermally metamorphosed shales	Siberia, Baykal Region	—	—	—	(1)	(3.3)	(1.2)	(5.1)	(0.9)	(4.6)	(0.75)	(2.1)	—	(1.4)	(0.27)	(25)	0.13	(< 1)	—	***
Pegmatoid diabases	Finland, Seppi	8.5×10^{-3}	2.7×10^{-2}	4.3×10^{-3}	1.5×10^{-2}	6.9×10^{-2}	1.7×10^{-3}	8.7×10^{-1}	2.6×10^{-3}	1.1×10^{-2}	3.5×10^{-3}	1.1×10^{-2}	2.6×10^{-3}	1.1×10^{-2}	1.8×10^{-3}	—	0.7	1.7	1.3×10^{-1}	[60]
Pegmatoid granite	Northern Karelia, Maarinvaary	8.5×10^{-4}	1.7×10^{-3}	4.3×10^{-4}	8.6×10^{-4}	5.2×10^{-4}	8.6×10^{-5}	6.9×10^{-1}	1.7×10^{-4}	8.7×10^{-4}	1.7×10^{-4}	7.0×10^{-4}	8.8×10^{-5}	5.3×10^{-4}	1.8×10^{-4}	4.0×10^{-3}	0.6	2.0	1.5×10^{-2}	[60]
Aplite	Tyan-Shan', Susamyr	1.0×10^{-3}	2.2×10^{-3}	—	2.0×10^{-3}	1.0×10^{-3}	—	1.3×10^{-1}	—	2.2×10^{-3}	—	1.5×10^{-3}	—	1.7×10^{-3}	—	1.5×10^{-2}	0.35	1.1	3.4×10^{-2}	Yu. A. Balashov
Eudialytite	Kola Peninsula, Lovozero	9.7×10^{-2}	2.3×10^{-1}	3.3×10^{-2}	1.5×10^{-1}	4.8×10^{-2}	—	5.3×10^{-2}	1.3×10^{-2}	7.2×10^{-2}	1.9×10^{-2}	4.5×10^{-2}	—	3.7×10^{-2}	—	5.0×10^{-1}	0.8	1.5	1.6	Same
Hydrothermally metamorphosed tuff breccia	Armeniya, Pambakskiy	4.1×10^{-2}	5.4×10^{-2}	3.1×10^{-3}	7.3×10^{-3}	8.8×10^{-4}	—	—	—	—	—	—	—	—	—	—	(40)	7.3	1.3×10^{-1}	Same
VIII. Metamorphic and sedimentary rocks																				
Phosphorite	Khoperoye	3.0×10^{-2}	4.0×10^{-2}	6.6×10^{-4}	5.3×10^{-3}	3.0×10^{-3}	5.0×10^{-4}	1.0×10^{-2}	1.7×10^{-3}	7.7×10^{-3}	1.7×10^{-3}	7.4×10^{-3}	1.2×10^{-3}	7.0×10^{-3}	1.3×10^{-3}	(6.0×10^{-2})	0.16	0.75	0.14	[34]
"	Yegor'yevskoye	7.2×10^{-3}	1.8×10^{-2}	2.3×10^{-3}	6.8×10^{-3}	1.4×10^{-3}	1.9×10^{-4}	1.0×10^{-3}	1.6×10^{-4}	5.9×10^{-4}	1.6×10^{-4}	4.0×10^{-4}	3.9×10^{-5}	3.1×10^{-4}	4.0×10^{-5}	(4.0×10^{-3})	5.5	2.7	0.05	[34]
Greenstone rocks	Southern Finnish Lapland	2.6×10^{-4}	6.0×10^{-3}	1.7×10^{-4}	4.3×10^{-4}	1.7×10^{-4}	—	1.7×10^{-4}	—	1.7×10^{-4}	—	8.5×10^{-5}	—	8.6×10^{-5}	—	8.7×10^{-4}	1.1	1.4	3.6×10^{-3}	[31]
Micaceous gneiss	Finland, Jehovaary	1.1×10^{-3}	2.8×10^{-3}	5.1×10^{-4}	2.4×10^{-3}	5.2×10^{-4}	—	7.8×10^{-4}	—	2.6×10^{-4}	—	1.7×10^{-4}	—	—	—	2.0×10^{-3}	2.0	1.2	1.3×10^{-2}	[61]
Quartzite	Southern Finnish Lapland	1.0×10^{-3}	1.4×10^{-3}	2.6×10^{-4}	9.4×10^{-4}	1.7×10^{-4}	—	2.6×10^{-4}	—	—	—	—	—	—	—	4.0×10^{-4}	4.0	1.5	5.3×10^{-3}	[31]
Shales	European Paleozoic	1.6×10^{-3}	3.4×10^{-3}	4.9×10^{-4}	2.8×10^{-3}	7.6×10^{-4}	1.2×10^{-4}	8.2×10^{-4}	1.0×10^{-4}	6.2×10^{-4}	1.9×10^{-5}	3.3×10^{-4}	2.6×10^{-5}	3.9×10^{-4}	1.1×10^{-4}	3.0×10^{-3}	1.8	1.2	1.9×10^{-2}	[54]
"	Japanese Paleozoic	1.7×10^{-3}	6.0×10^{-3}	6.1×10^{-4}	2.3×10^{-3}	6.2×10^{-4}	9.5×10^{-5}	4.9×10^{-4}	1.1×10^{-4}	3.8×10^{-4}	8.7×10^{-4}	1.9×10^{-5}	1.3×10^{-5}	1.3×10^{-4}	4.8×10^{-5}	2.6×10^{-3}	2.6	2.6	2.0×10^{-2}	[54]
Shales rich in aluminum	Southern Finnish Lapland	1.6×10^{-3}	2.4×10^{-3}	4.3×10^{-4}	1.3×10^{-3}	3.5×10^{-4}	—	4.4×10^{-4}	—	2.6×10^{-4}	—	1.7×10^{-4}	—	1.7×10^{-4}	—	1.3×10^{-3}	2.8	1.8	1.0×10^{-2}	[31]
Paleogenic clay	Kazakhstan	(0.2)	(0.6)	(0.19)	(1)	(0.5)	—	(0.35)	(0.10)	(0.42)	—	(0.12)	—	(0.08)	—	(1.2)	1.0	0.6	—	[36]***
C_1 clay	Russian Platform, Malinkovskiy	3.7×10^{-3}	8.5×10^{-3}	1.2×10^{-3}	5.0×10^{-3}	1.4×10^{-3}	—	1.5×10^{-3}	—	1.1×10^{-3}	—	1.0×10^{-3}	—	—	—	—	1.4	1.7	4.1×10^{-2}	Yu. A. Balashov
"	Tovarkovo	6.7×10^{-3}	1.3×10^{-2}	1.7×10^{-3}	6.7×10^{-3}	1.5×10^{-3}	—	1.3×10^{-3}	4.7×10^{-4}	1.0×10^{-3}	2.0×10^{-4}	7.3×10^{-4}	—	6.5×10^{-4}	—	7.5×10^{-3}	2.5	2.0	4.9×10^{-2}	Same
C_1 sandstone	Povarovka	3.9×10^{-3}	8.6×10^{-3}	1.3×10^{-3}	5.3×10^{-3}	1.6×10^{-3}	—	1.6×10^{-3}	—	1.4×10^{-3}	—	—	—	—	—	—	(1.5)	1.6	4.3×10^{-2}	Same
D_2 carbonates	Lyskovo	(0.9)	(1.8)	—	(1.0)	(0.23)	—	(0.29)	—	(0.21)	—	(0.15)	—	—	—	(1.4)	1.8	1.8	—	***
Limestone	New Mexico	6×10^{-4}	1×10^{-3}	1.0×10^{-4}	3.0×10^{-4}	8×10^{-5}	—	6×10^{-5}	—	4×10^{-5}	1×10^{-5}	5×10^{-5}	1×10^{-5}	1×10^{-5}	—	—	(3.5)	3.3	(3.0×10^{-3})	[67]
IX. Average for individual massifs and the earth's crust																				
Earth's crust		2.9×10^{-3}	7.0×10^{-3}	9×10^{-4}	3.7×10^{-3}	8×10^{-4}	1.3×10^{-4}	8×10^{-4}	4.3×10^{-4}	5×10^{-4}	1.7×10^{-4}	3.3×10^{-4}	2.7×10^{-5}	3.3×10^{-4}	8×10^{-5}	2.9×10^{-3}	2.8	1.9	2.5×10^{-2}	[23]
Batholite of granitoids	Central Tyan-Shan', Susamyr	8.7×10^{-3}	1.6×10^{-2}	1.9×10^{-3}	6.4×10^{-3}	1.1×10^{-3}	—	7.8×10^{-4}	—	7.3×10^{-4}	—	4.0×10^{-4}	—	3.8×10^{-4}	—	4.2×10^{-3}	4.7	2.5	4.8×10^{-2}	Yu. A. Balashov
Alkaline massif	Kola Peninsula, Lovozero	3.6×10^{-2}	6.7×10^{-2}	7.4×10^{-3}	2.7×10^{-2}	4.8×10^{-3}	1.0×10^{-3}	4.2×10^{-3}	9.3×10^{-4}	4.0×10^{-3}	8.8×10^{-4}	2.1×10^{-3}	3.5×10^{-4}	1.8×10^{-3}	3.4×10^{-4}	2.1×10^{-2}	4.0	2.5	2.1×10^{-1}	[7]
"	Central Tyan-Shan', Sandyk	4.9×10^{-3}	9.3×10^{-3}	1.1×10^{-3}	4.4×10^{-3}	9.0×10^{-4}	—	7.0×10^{-4}	—	4.8×10^{-4}	—	3.0×10^{-4}	—	3.0×10^{-4}	—	3.1×10^{-3}	4.7	2.1	3.0×10^{-2}	[28]

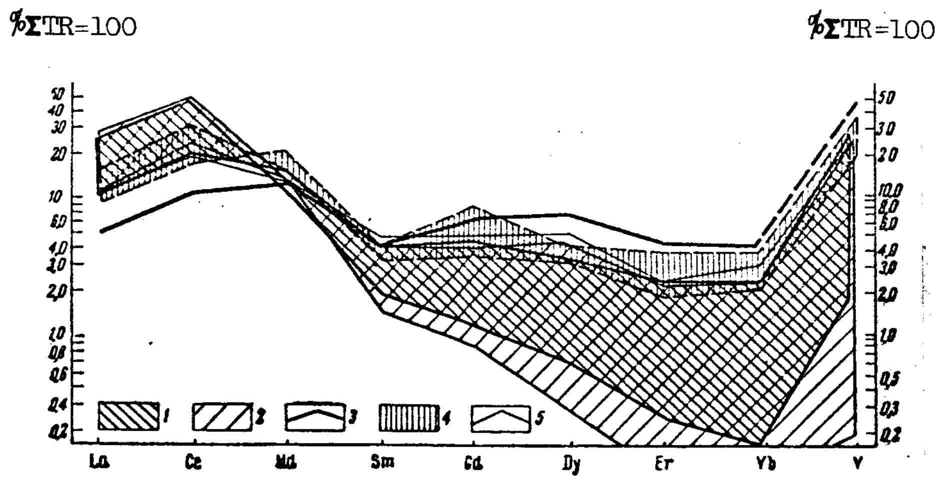
NOTE. Since the majority of analyses of rare earth elements were published recently [2, 3, 7, 8, 28], only typical and new data are included in the table. Some still unpublished data on Western Tuva Autonomous Oblast' kindly presented by A.S. Pavlenko have also been used in the table.

*Unpublished data from A.S. Pavlenko and N.V. Turanskaya.

**The figures for alkaline ultrabasic rocks were calculated in accordance with determinations of rare earth elements in minerals.

***The values for individual rare earth elements were given in provisional units, taking Nd = 1, since the content of rare earth elements is not known.

[1]Numbers in brackets refer to references at end of paper.



Variations in composition of TR (rare earth elements) in different types of igneous rocks.

1 - Granites; 2 - syenites and nepheline syenites; 3 - meteorites (chondrites); 4 - gabbro and gabbro diorites; 5 - peridotite.

At the same time, a relative concentration of the yttrium group is observed in ultrabasic and basic rocks ($\Sigma Ce/\Sigma Y$ = 1.0-1.2).

3. The content of rare earth elements increases as we go from ultrabasic and basic rocks (10^{-4}-10^{-3} percent) to acid rocks ($n \cdot 10^{-2}$ percent) by more than an order of magnitude.

It is probable that these differences in the composition and content of rare earth elements in the principal types of rocks characterize to a certain extent the process of separation of rare earth elements in the geochemical evolution of the earth, which was pointed out by A. P. Vinogradov (Refs. 21, 22).

A relative accumulation of ΣY in the more melanocratic intrusive phases was noted in certain alkaline massifs (Refs. 7, 28). In the Susamyr batholite of granitoid rocks an early phase made up of gabbro-diorites, diorites, and gabbro was comparatively rich (according to our data) in the yttrium group as compared with a later phase of granites ($\Sigma Ce/\Sigma Y$ = 2.0 and 5.8, respectively).

Even though the processes which cause such separation of rare elements in individual massifs and in the earth's crust as a whole have not been studied, the attraction of the yttrium group of rare earth elements to the more basic rocks can be explained in the first approximation by the effect of the crystallochemical factor. Comparison of the distribution of rare earth elements and scandium, an element close to the yttrium group of rare earth elements in respect to chemical and crystallochemical properties, still serves as the basis for this opinion.

It is known (Refs. 9, 10, 21, 23, 26) that scandium accumulates noticeably in ultrabasic and basic rocks due to isomorphic replacement of Mg^{2+} and Fe^{2+} in olivines and pyrozenes. A like isomorphism can also be assumed for the yttrium group of rare earth elements (the discrepancy in the sizes of the ionic radii of the yttrium group and of Mg^{2+}, Fe^{2+} does not exceed 30 percent and is comparable with the difference in the isomorphism of Na and K in feldspars and Mg and Ca in certain clinopyroxenes (Ref. 51).

4. In contrast to the accumulation of the cerium group of rare earth elements in the ultrabasic rock - basic rock - granite series, many geochemical processes are marked by the accumulation of the yttrium group of rare earth elements in the final stages.

/106

A pronounced concentration of the yttrium group of rare earth elements was encountered in certain hydrothermal formations and pegmatites ($\Sigma Ce/\Sigma Y$ = 0.1-0.7), in aplites ($\Sigma Ce/\Sigma Y$ = 0.35), and in individual deposits of phosphorites ($\Sigma Ce/\Sigma Y$ = 0.16). However, the rocks listed here occupy an insignificant volume as compared with the principal types of igneous and sedimentary rocks.

5. A few analyses of shales, clays, sandstones, and limestones indicate that elements of the cerium group predominate in these rocks.

6. A comparison of the ratios of rare earth elements in granites, ultrabasic, and basic, sedimentary and alkaline rocks with the composition of rare earth elements in the silicate phase of chondrites indicates that on the whole the composition of rare earth elements in the rocks of the earth's crust is distinguished by a high relative content of the cerium group ($\Sigma Ce/\Sigma Y$ = 1.0-30, on the average $\Sigma Ce/\Sigma Y$ = 2.5-3.0), which differs sharply from the ratios of rare earth elements in meteorites ($\Sigma Ce/\Sigma Y$ = 0.5-0.6) in which the yttrium group predominates.

The content of rare earth elements in the rocks of the earth's crust (with fluctuations from $9 \cdot 10^{-4}$ to $6.0 \cdot 10^{-1}$ percent TR_2O_3 and more) is significantly higher than in meteorites (5 to $7 \cdot 10^{-4}$ percent TR_2O_3).

Before going on to analysis of the differences in composition and content of rare earth elements in the earth's crust and in meteorites, it is necessary to discuss the nature of the correlation ratios of rare earth elements in rocks.

Correlation Ratios of Rare Earth Elements in Rocks.

As previously noted, simple correlation connections whose mathematical expression was given in empirical equations derived by Masuda (Ref. 53) and Turanskaya (Ref. 37) were established for minerals as a result of investigations from 1953 through 1958. Such connections are considered for rocks in accordance with analyses known at the present time.

It can be seen from the figure that the maximum fluctuations in the content of individual rare earth elements in different types of rocks are to be found in the lightest and the heaviest lanthanides, chiefly on both sides of Nd, whose relative content in rocks (and in meteorites) remains almost constant (12-16 percent where TR = 100, Table 2), in spite of sharp changes in the total content of other rare earth elements. It is probable that the latter may serve as the basis for a natural geochemical boundary between the cerium and yttrium groups of rare earth elements when computing the $\Sigma Ce/\Sigma Y$ ratio.

This stability in the Nd content in different types of rocks when there are significant changes in the composition of rare earth elements also permits one to make use of Nd as a unique standard for comparisons inside a group of rare earth elements. The La/Nd, Ce/Nd, Pr/Nd, ratios, etc., should characterize the rare earth composition of a rock just as well as the $\Sigma Ce/\Sigma Y$ ratio and can also be comparable in respect to the absolute value for different types of rocks, including meteorites (with accuracy of $\pm$ 20 percent, Table 2).

In a number of cases however, it is necessary to reconstruct ratios of rare earth elements in rocks in which only certain rare earth elements were determined by analysis.

A correspondence between changes in the ratios of individual rare earth elements and variations in the total composition of rare earth elements (in particular, for Ce/Nd and Er/Nd to the $\Sigma Ce/\Sigma Y$ ratio (Ref. 3) was established in investigations of the distribution of rare earth elements in different alkaline massifs (Refs. 3, 7, 28) and in the Susamyr batholith.

Some examples which illustrate the presence of correlation ratios for rare earth elements are presented in Table 3. As can be seen, ratios of neighboring pairs of elements (La/Ce, Ce/Pr, Pr/Nd, etc.) undergo directed changes: the ratios of neighboring pairs decrease with relative /108

Table 2. Fluctuations in the Relative Content of Individual Rare Earth Elements in Rocks (TR = 100)

Element	Silicate Phase of Meteorites	Peridotite	Granite	Granite	Granite	Granite	Tawite	Lujaurite	Fluctuations in Content
La	6.2	10.4	9.7	16.2	22	27.6	30	28	6.2-30
Ce	9.9	19.2	19.8	31	40.5	44.5	47	50	9.9-50
Pr	2.3	3.5	3.8	3.4	4.8	4.0	4.2	4.6	2.3-4.8
Nd	12.1	14.0	15.9	13.7	15.7	12.1	14.8	13.3	12.1-15.9
Sm	4.2	5.0	4.0	3.4	2.6	2.0	1.3	1.4	1.3-5.1
Gd	6.5	5.2	4.3	3.1	1.7	1.3	0.45	0.8	0.45-6.5
Dy	6.9	5.5	3.5	2.8	1.6	1.0	0.30	0.3	0.3-6.9
Ho	1.5	1.4	0.5	1.1	-	-	-	-	0.5-1.5
Er	4.0	2.7	2.4	1.9	0.8	0.5	-	-	0.5-4.0
Yb	3.7	3.3	2.4	1.9	0.75	0.35	-	-	0.3-3.7
Y	(40)	27	32	19	8.6	6.0	-	-	6.0-(40)
$\frac{\Sigma Ce}{\Sigma Y}$	0.5	1.1	1.2	2.0	5.8	9.2	(39)	(48)	0.5-(48)

Table 3. Correlation Ratios of Rare Earth Elements in Igneous Rocks

Rock or Phase	ΣCe/ΣY	La–Pr/TR, %	La/Ce	Ce/Pr	Pr/Nd	Nd/Sm	Sm/Eu	Eu/Gd	Gd/Tb	Tb/Dy	Dy/Ho	Ho/Er	Er/Tu	Tu/Yb	Yb/Lu	Ce/Nd	Sm/Gd	Gd/Dy	Dy/Er	Er/Yb	Y/Er
The eudialytic complex of the Lovozero Massif																					
Tawite	39	82	0.66	11.5	0.28	11	--	—	—	—	—	—	—	—	—	3.2	3.0	1.5	—	—	—
Porphyraceous juvite	19	78	0.62	9.7	0.30	10	--	—	—	—	—	—	—	—	—	2.9	1.7	1.5	4.0	—	—
Eudialytic lujaurite with loparite	5.3	68	0.60	9.3	0.30	7.7	--	—	—	—	—	—	—	—	—	2.8	1.0	1.2	1.8	1.5	11.5
same	4.5	65	0.56	9.0	0.29	5.9	--	—	4.9	0.20	3.8	0.57	—	—	—	2.6	1.4	0.8	2.1	[illegible]	11 5
Eudialytic and porphyraceous jujaurites	1.8	44	0.48	7.7	0.24	3.6	7.0	0.16	3.6	0.24	3.4	0.55	6.0	0.17	4.3	1.8	1.1	0.9	1.9	1.0	10
Eudialytite	0.8	28	0.43	6.8	0.22	3.1	--	—	3.9	0.19	3.7	0.43	—	—	—	1.5	0.9	0.7	1.6	1.2	11
The differentiated complex of the Lovozero Massif																					
Melanocratic lujaurite	48	83	0.60	10.6	0.35	11	--	—	—	—	—	—	—	—	—	3.7	1.9	2.0	—	—	—
Urtite, 4th and 3rd horizons	24	81	0.58	10.5	0.34	10	--	—	—	—	—	—	—	—	—	3.6	1.6	1.2	3.0	2.0	—
Foyaite, 4th horizon	10	73	0.52	10.0	0.29	7.2	--	—	—	—	—	—	—	—	—	2.9	1.4	0.9	3.7	—	10
Differentiated complex (average)	5.7	67	0.55	9.4	0.28	6.8	6.5	0.18	5.2	0.22	5.8	0.33	7.5	0.17	6,0	2.6	1.1	1.2	1.9	1.3	10
Foyaite of the lower horizon	1.8	48	0.57	9.2	0.25	4,4	--	—	7.0	0.17	2.9	0.47	—	—	—	2.3	0.8	1.2	1.3	0.8	10
The Sandyk Massif																					
Nepheline	11	92	0.56	8.9	0.28	7.1	--	—	—	—	—	—	—	—	—	2.5	1.6	1.5	2.0	—	—
Alkaline syenite	4.9	83	0.52	8.8	0.26	5.0	--	—	—	—	1,6	1,0	—	—	—	2.3	1.7	1.5	1.6	—	12
Alkaline earth syenite	3.8	79	0.50	8.7	0.23	4.8	--	—	2.7	0.6	—	—	—	—	—	2.0	1.3	1.6	1.4	1.4	—
Alkaline gabbroids	2.9	74	0.47	8.3	0.23	4.3	--	—	—	—	—	—	—	—	—	1.9	1.1	1.4	1.4	0.7	—
The Susamyr Batholith																					
Porphyraceous granites, second phase	5,8	68	0,54	8.5	0.30	6.0	—	—	—	—	—	—	—	—	—	2.6	1.6	1.1	2.0	1.1	10.5
Leucocratic granites, third phase	2,0	51	0.52	8.6	0.26	4.1	—	—	3.8	0.29	—	—	—	—	—	2.3	1.1	1.1	1.5	1.0	10
Aplites	0,3	12	0,45	—	—	2.0	—	—	—	—	—	—	—	—	—	1.1	0.8	0.6	1.5	0.9	10
The silicate phase of chondrite and peridotite																					
Peridotite	1,1	33	0.55	5.5	0.25	2,8	--	—	4.8	0.20	4.0	0,51	—	—	—	1.4	1,0	0.95	2.0	0.85	10
Silicate phase of chondrite	(0.55)	18	0,60	4.3	0,19	2.9	2.6	0.25	6.7	0,14	4.9	0,36	5.5	0.20	5.4	0,82	0.65	0.9	1.7	1.1	—

concentration of the yttrium group in rocks or phase; that is, in each pair there is a shift toward an increasing role of the heavier lanthanide.

It should be noted that although changes in the ratios of neighboring pairs are clear in the case of light rare earth elements, we have too little data to be able to speak confidently of such changes in the case of the yttrium group. Therefore, we have also utilized comparisons of pairs of neighboring even rare earth elements in Table 3 which show a regular change similar to variations in the ratios of neighboring pairs of elements.

Thus, in principle, any ratio of two rare earth elements corresponds to the composition of rare earth elements in a rock (or phase), expressed in any form ($\Sigma Ce/\Sigma Y$ or $\Sigma La + Ce + Pr$, etc.); that is, the ratio of a pair of rare earth elements changes in a completely defined manner with a change in the total composition of rare earth elements.

A knowledge of the correlation ratios of rare earth elements permits one to reconstruct the composition of rare earth elements in respect to the ratios and contents of individual elements; to detect errors in computations or analyses of rare earth elements; and to establish deviations from normal ratios, etc.

A number of examples with use of correlation ratios are given in Table 4.

a) The approximate composition of rare earth elements in dunite is calculated in accordance with known data for Eu (1.10^{-6} percent) and Dy ($5 \cdot 10^{-6}$ percent, Ref. 21) with analyses of rare earth elements in the silicate phase of chondrites (Ref. 63), carried out by the same method used in determining Eu and Dy in dunite, cited for purposes of comparison.

b) In many cases when analyzing rare earth elements in minerals and rocks it was possible to determine the content of only the most prevalent rare earth elements. The cerium group was usually almost completely represented while data were, to a large extent, lacking on the yttrium group. The latter is the reason why the content of heavy lanthanides is artificially reduced in computations of the average composition of rare earth elements in minerals and in rocks.

The table shows two compositions of rare earth elements as computed by different authors in accordance with the balance of rare earth elements in minerals: the average for ultrabasic alkaline intrusions in the Kola Peninsula, after Kukharenko and others (1960, Ref. 29) and the ratio of rare earth elements in granite from the Ukrainian crystalline shield, after Gavrilova and Turanskaya (Ref. 24). The cited examples are characterized by sharply reduced concentrations of the yttrium group, which is readily discovered in the lack of correspondence between the average ratios $\Sigma Ce/\Sigma Y$ = 14-35 and the ratios of pairs of elements La/Nd = 0.75-1.3 or Ce/Nd = 1.8-2.5, etc. (according to Table 3 of correlation ratios of rare earth elements).

Checking the composition of rare earth elements in granite from the /111 Ukrainian crystalline shield by direct X-ray spectral analysis of rare earth elements, carried out with N. V. Turanskaya participating, showed that the composition of rare earth elements in this granite was actually characterized by a $\Sigma Ce/\Sigma Y$ = 4.7 ratio (and not $\Sigma Ce/\Sigma Y$ = 14, as computed from the mineralogical balance). An analysis of rapakivi granite from the same area ($\Sigma Ce/\Sigma Y$ = 5.8, Table 4) confirmed the accuracy of the preliminary estimate (based on the table of correlation ratios) of the computational reduction of the relative content of the yttrium group made by the authors.

c. Table 4 also gives analyses of sphene-amphibolitic ijolite-melteigites from the Lovozero Massif in which an unusual ratio of rare earth elements was discovered (reduced La/Nd, Ce/Nd, and Pr/Nd ratios as compared with other widely prevalent rocks in the massif which have close values of $\Sigma Ce/\Sigma Y$ - eudialytic lujaurite with titanates and sodalitic syenite). The deviation of the composition of rare earth elements in ijolite-melteigites from the normal correlation ratios indicated an unusual genesis for these rocks. On the basis of peculiarities of chemical and mineralogical composition and the geological position (in zones where xenoliths from Devonian effusions are prevalent), Gerasimovskiy and Polyakov (Ref. 25) suggest that processes of assimilation and hybridism played a large role in the formation of ijolite-melteigites. A comparison of the composition of rare earth elements in these rocks with the ratio of rare earth elements in the Devonian xenolith and the average in eudialytic lujaurites which enclose these rocks confirms this viewpoint since the composition of rare earth elements in ijolite-melteigite turns out to be "intermediate" between the sharply ceric composition of rare earth elements in the xenolith and the composition of rare earth elements in eudialytic lujaurites with concentration of the yttrium group.

These examples show the importance of knowing the correlation ratios of rare earth elements in analyzing the composition of rare earth elements in rocks.

In conclusion, it is necessary to point out the need for taking into account yttrium in the composition of rare earth elements. The Y/Er ratio is presented in Table 3. As can be seen there, this ratio changes comparatively little (10-12) for different types of rocks, which indicates the generality of routes of migration for rare earth elements and yttrium in the magmatic process and permits rough computation of the yttrium content in rocks when data are lacking in respect to this element.

Table 4. Examples of Computation and Analysis of the Composition of Rare Earth Elements in Rocks by Correlation Ratios of Rare Earth Elements (the Content of Rare Earth Elements is Given in Percent and in Relative Quantities with Nd = 1)

Element	Nanshan Dunite			Alkaline Ultrabasic Rocks of the Kola Peninsula				Kirovograd Granite (Ukrainia)				Rapakivi Granite (Ukrainia) Analysis		Analyses of Rocks from the Lovozero Alkaline Massif (Nd=1)					
	A. P. Vinogradov [21]	Computations		A. A. Kukharenko and others [29]		Computations		L. K. Gavrilova, N. V. Turanskaya [21]		Analysis				Sphene-Amphibolitic Ijolite-Melteigites		Eudialytic Lujaurite with Titanates	Sodalitic Syenite	Xenolith from a Devonian Effusion	Eudialytic Lujaurites
	%	%	Nd=1	%	Nd=1	%	Nd=1	%	Nd=1	%	Nd=1	%	Nd=1	№ 2953	№ 850				
La	—	$2.9 \cdot 10^{-6}$	0.44	$3.6 \cdot 10^{-2}$	1.2	$3.8 \cdot 10^{-2}$	1.3	$6.8 \cdot 10^{-3}$	1.3	$6.6 \cdot 10^{-3}$	0.9	$9.0 \cdot 10^{-3}$	0.9	1.0	0.9	1.7	1.5	1.3	0.9
Ce	—	$6.9 \cdot 10^{-6}$	1.1	$7.5 \cdot 10^{-2}$	2.6	$7.5 \cdot 10^{-2}$	2.6	$1.5 \cdot 10^{-2}$	2.5	$1.5 \cdot 10^{-2}$	2.0	$1.9 \cdot 10^{-2}$	2.0	1.9	1.8	2.8	2.3	2.4	1.8
Pr	—	$1.2 \cdot 10^{-6}$	0.18	$7.7 \cdot 10^{-3}$	0.27	$7.7 \cdot 10^{-3}$	0.27	$1.3 \cdot 10^{-3}$	0.25	$1.9 \cdot 10^{-3}$	0.25	$2.3 \cdot 10^{-3}$	0.24		0.25	0.30	0.26	0.27	0.24
Nd	—	$6.6 \cdot 10^{-6}$	1	$2.9 \cdot 10^{-2}$	1	$2.9 \cdot 10^{-2}$	1	$5.1 \cdot 10^{-3}$	1	$7.6 \cdot 10^{-3}$	1	$9.5 \cdot 10^{-3}$	1	1	1	1	1	1	1
Sm	—	$2.4 \cdot 10^{-6}$	0.36	$3.0 \cdot 10^{-3}$	0.10	$3.5 \cdot 10^{-3}$	0.12	$9.5 \cdot 10^{-4}$	0.18	$1.5 \cdot 10^{-3}$	0.20	$1.8 \cdot 10^{-3}$	0.19	0.20	0.22	0.15	0.19	0.17	0.28
Eu	$1 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	0.15	$8.8 \cdot 10^{-4}$	0.03	$6.0 \cdot 10^{-4}$	0.02	—		—		—		—	—	—	—	—	0.04
Gd	—	$4.2 \cdot 10^{-6}$	0.64	$1.6 \cdot 10^{-3}$	0.06	$2.9 \cdot 10^{-3}$	0.10	$5.6 \cdot 10^{-4}$	0.11	$8.6 \cdot 10^{-4}$	0.11	$1.2 \cdot 10^{-3}$	0.13	0.13	0.17	0.13	0.12	0.11	0.24
Tb	—	$6.7 \cdot 10^{-7}$	0.10	$2.4 \cdot 10^{-5}$	0.003	$8.0 \cdot 10^{-4}$	0.03	$1.3 \cdot 10^{-5}$	0.002	$2.7 \cdot 10^{-4}$	0.04			—	0.03	—	—	—	0.07
Dy	$5 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	0.77	$3.9 \cdot 10^{-4}$	0.013	$2.0 \cdot 10^{-3}$	0.07	$1.4 \cdot 10^{-4}$	0.03	$8.4 \cdot 10^{-4}$	0.11	$9.5 \cdot 10^{-4}$	0.10	0.08	0.11	0.11	0.10	0.08	0.27
Ho	—	$1.1 \cdot 10^{-6}$	0.17	$3.1 \cdot 10^{-5}$	0.001	—		$2.0 \cdot 10^{-5}$	0.004	—		—		—	0.04		—	—	0.08
Er	—	$3.2 \cdot 10^{-6}$	0.49	$6.3 \cdot 10^{-5}$	0.002	$1.1 \cdot 10^{-3}$	0.04	$5.3 \cdot 10^{-5}$	0.01	$3.8 \cdot 10^{-4}$	0.05	$2.0 \cdot 10^{-4}$	0.02	0.03	0.02	0.06	0.07	0.04	0.14
Tu	—	$6.0 \cdot 10^{-7}$	0.09	$7.8 \cdot 10^{-6}$	0.001	—		—		—		—		—	—	—	—	—	0.02
Yb	—	$3.1 \cdot 10^{-6}$	0.47	$1.2 \cdot 10^{-4}$	0.004	$8.0 \cdot 10^{-4}$	0.03	$1.8 \cdot 10^{-5}$	0.003	$3.6 \cdot 10^{-4}$	0.05	$1.9 \cdot 10^{-3}$	0.02		0.03	0.04		—	0.14
Lu	—	$6.2 \cdot 10^{-7}$	0.10	$3.1 \cdot 10^{-5}$	0.001	—		$2.8 \cdot 10^{-6}$	—	—		—		—	—	—	—	—	0.03
Y	—	$2.9 \cdot 10^{-5}$	4.4	$2.0 \cdot 10^{-3}$	0.07	$1.1 \cdot 10^{-2}$	0.40	$3.4 \cdot 10^{-4}$	0.10	$3.8 \cdot 10^{-3}$	0.5	$2.0 \cdot 10^{-3}$	0.20	0.3	0.4	0.7	—	0.5	1.5
TR_2O_3	—	$8 \cdot 10^{-5}$		$1.8 \cdot 10^{-1}$		$2.0 \cdot 10^{-1}$		$3.3 \cdot 10^{-2}$		$4.6 \cdot 10^{-2}$		$5.5 \cdot 10^{-3}$		—	—	—	—	—	—
$\frac{\Sigma Ce}{\Sigma Y}$	—	0.4		35		8		14		4.7		5.8		7.2	5.1	5.3	4.6	6.6	1.8

The Deficit of the Yttrium Group of Rare Earth Elements in the Earth's Crust as Compared with That of Meteorites (Chondrites)

This difference in the composition and content of rare earth elements in the earth's crust and in meteorites is obviously connected with processes which took place during the formation of the earth's crust. The essential nature and basic trends of these processes have been examined in the works of A. P. Vinogradov.

The basic hypothesis in the ideas developed by A. P. Vinogradov is "recognition that the chemical composition of the earth's mantle is analogous to the composition of the matter in meteorites...." "more precisely, the composition of the silicate phase of the earth corresponded to the composition of stony meteorites" (Ref. 20).

According to A. P. Vinogradov, the formation of the earth's crust is the result of melting of basaltic matter from the mantle. Differentiation of the mantle is expressed in separation into high-temperature dunites and a less refractory basaltic phase; in addition, rare earth elements are characterized by an increase in their content in the dunite-chondrite-basalt series (Ref. 21).

Starting with this scheme of the melting of the mantle and taking into account the difference in the composition of rare earth elements in meteorites and in the earth's crust, one may assume that when the matter in the mantle split into a high-temperature phase of abyssal rock and a basaltic residue from which the earth's crust was formed, there was also a separation of rare earth elements. Since the rocks in the earth's crust show a sharp concentration of the cerium group of rare earth elements as compared with the composition of rare earth elements in the sil- /112
icate phase of meteorites (the matter in the mantle), one must expect a relative accumulation of the yttrium group of rare earth elements in the abyssal differentiates of the mantle (possibly in dunites too).

At present there are no data on the composition of rare earth elements in abyssal rocks. A very approximate estimate of the composition of rare earth elements in dunites can be obtained only by single analyses of Eu and Dy (Ref. 21) and making use of the Eu/Dy ratio.

If we accept this ratio, then a decrease in it will correspond to a relative concentration of the yttrium group and an increase in an accumulation of the cerium group of rare earth elements in the rare earth composition of rocks (according to correlation ratios of rare earth elements in rocks).

Data on determination of Eu and Dy and their ratio in certain rocks of the earth's crust, meteorites, and dunites are presented in Table 5. As can be seen in the table, the lowest value for the Eu/Dy ratio = 2 is

Table 5

Changes in the Eu/Cy Ratio from Dunites to Meteorites and the Earth's Crust

Phase or Rock	Content		Eu/Dy	Author
	Eu, %	Dy, %		
Dunite	$1.0 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	0.20	A. P. Vinogradov (Ref. 21)
Chondrite	$8.7 \cdot 10^{-6}$	$3.9 \cdot 10^{-5}$	0.22	R. A. Schmitt and others (Ref. 63)
Same	$8.0 \cdot 10^{-6}$	$3.4 \cdot 10^{-5}$	0.24	Same
Same	$1.0 \cdot 10^{-6}$	$3.0 \cdot 10^{-5}$	0.34	A. P. Vinogradov (Ref. 21)
Granite	$1.1 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	0.37	Same (Ref. 21)
Basalt	$1.3 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	0.52	Same (Ref. 21)
Earth's crust	$1.3 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	0.26	Same (Ref. 23)

observed in dunites; that is, we should expect a relative predominance of the yttrium group in dunites, as compared with meteorites and rocks of the earth's crust. Computation of the composition of rare earth elements by the same data (Table 4) shows that a $\Sigma Ce/\Sigma Y = 0.4$ ratio is probable in dunites while $\Sigma Ce/\Sigma Y = 0.5\text{-}0.6$ is observed in meteorites, and still higher in the rocks of the earth's crust.

Thus, we can assume, as yet from indirect data and calculations, that the difference in composition of rare earth elements in the earth's crust and in the silicate phase of chondrites (the relative deficit of the yttrium group of rare earth elements in the earth's crust) is due chiefly to dispersion of yttrium rare earth elements in Fe- and Mg- silicates of abyssal rocks in the mantle even though the composition of rare earth elements in these rocks and in meteorites is apparently not too different.

References

1. Balashov, Yu. A. and Turanskaya, N. V. Geokhimiya, No. 7, 1960.
2. Balashov, Yu. A. and Turanskaya, N. V. Geokhimiya, No. 8, 1960.
3. Balashov, Yu. A. and Turanskaya, N. V. Geokhimiya, No. 12, 1961.
4. Balashov, Yu. A. and Khitrov, L. M. Geokhimiya, No. 9, 1961.
5. Balashov, Yu. A. Sb. Metody opredeleniya i analiza redkikh elementov (Methods for Determination and Analysis of Rare Earth Elements) (Collected Articles), Moscow, Izdalel'stvo AN SSSR, 1961.
6. Balashov, Yu. A. and Turanskaya, N. V. Sb. Redkozemel'nyye elementry (Rare Earth Elements) (Collected Articles), in press.
7. Balashov, Yu. A. Geokhimiya, No. 3, 1962.
8. Balashov, Yu. A. and Turanskaya, N. V. Geokhimiya, No. 4, 1962.
9. Borisenko, L. F. Geokhimiya, No. 7, 1959.
10. Borisenko, L. F. and Rodionov, D. A. Geokhimiya, No. 9, 1961.
11. Borodin, L. S. and Barinskiy, R. L. Geokhimiya, No. 4, 1960.
12. Borodin, L. S. Geokhimiya, No. 6, 1960.
13. Vaynshteyn, E. Ye., Tugarinov, A. I. and Turanskaya, N. V. Doklady AN SSSR, Vol. 104, No. 2, 1955.
14. Vaynshteyn, E. Ye., Tugarinov, A. I. and Turanskaya, N. V. Doklady AN SSSR, Vol. 106, No. 4, 1956.
15. Vaynshteyn, E. Ye., Tugarinov, A. I. and Turanskaya, N. V. Geokhimiya, No. 2, 1956.
16. Vaynshteyn, E. Ye., Pavlenko, A. S., Turanskaya, N. V. and Yulova, T. S. Geokhimiya, No. 12, 1961.
17. Vernadskiy, V. I. Doklady AN SSSR, Seriya A, No. 2, 1929.
18. Vinogradov, A. P. Geokhimiya redkikh i rasseyannykh khimicheskikh elementov v pochvakh (The Geochemistry of Rare and Trace Elements in Soils), Moscow, Izdatel'stvo AN SSSR, 1950.
19. Vinogradov, A. P. Geokhimiya, No. 1, 1956.
20. Vinogradov, A. P. Khimicheskaya evolyutsiya Zemli (The Chemical Evolution of the Earth), Moscow, Izdatel'stvo AN SSSR, 1959.
21. Vinogradov, A. P. Geokhimiya, No. 1, 1961.
22. Vinogradov, A. P. Izvestiya AN SSSR, Seriya geologicheskaya, No. 7, 1961.
23. Vinogradov, A. P. Geokhimiya, No. 7, 1962.
24. Gavrilova, L. K. and Turanskaya, N. V. Geokhimiya, No. 2, 1958.
25. Gerasimovskiy, V. I. and Polyakov, A. I. Doklady AN SSSR, Vol. 143, No. 5, 1962.
26. Dudynina, A. S. Institute of Geology of Mineral Deposits, Petrography and Geochemistry (IGEM) AN SSSR, No. 46, Moscow, 1960.
27. Zaykovskiy, F. V. and Bashmakova, V. S. Zhurnal analiticheskoy khimii, Vol. 14, No. 1, 1959.
28. Zlobin, B. I. and Balashov, Yu. A. Geokhimiya, No. 9, 1961.

29. Kukharenko, A. A. and others. Kaledonskiy kompleks ul'traosnovnykh shchelochnykh porod Kol'skogo poluostrova (The Caledonian Complex of Ultrabasic Alkaline Rocks of Kola Peninsula), Report of the All-Union Geological and Scientific Research Institute (VSEGEI), 1960.
30. Nockolds, S. R. and Allen, R. Geokhimicheskiye nablyudeniya (Geochemical Observations), Moscow, Izdatel'stvo inostrannoy literatury, 1958.
31. Sahama, T. G. Sb. Redkiye elementy v izverzhennykh gornykh porodakh i mineralakh (Rare Elements in Igneous Rocks and Minerals) (Collected Articles), Moscow, Izdatel'stvo inostrannoy literatury, 1952.
32. Semenov, Ye. I. and Barinskiy, R. L. Geokhimiya, No. 4, 1958.
33. Semenov, Ye. I. Geokhimiya, No. 5, 1958.
34. Semenov, Ye. I. and others. Geokhimiya, No. 5, 1962.
35. Pavlenko, A. S., Vaynshteyn, E. Ye. and Turanskaya, N. V. Geokhimiya, No. 4, 1959.
36. Tugarinov, A. I. and Vaynshteyn, E. Ye. Sb. Geokhimicheskiye tsikly (Geochemical Cycles) (Collected Articles). Paper given before the Council of Geologists at the International Geological Congress, Session XXI, Problem I; Moscow, Izdatel'stvo AN SSSR, 1960.
37. Turanskaya, N. V. Razrabotka metodov rentgenospektral'nogo analiza redkozemel'nykh elementov i ikh primeneniye dlya geokhimii (Development of Methods for X-ray Spectral Analysis of Rare Earth Elements and Their Application in Geochemistry) (Candidate's Dissertation), Geokhimiya (GEOKHI), AN SSSR, 1958.
38. Fersman, A. Ye. Geokhimiya (Geochemistry), Vol. IV, Leningrad, Khimteoretizdat, 1939.
39. Haberlandt, C. Sb. Redkiye elementy v izverzhennykh gornykh porodakh i mineralakh (Rare Elements in Igneous Rocks and Minerals) (Collected Articles), Moscow, Izdatel'stvo inostrannoy literatury, 1962.
40. Hevesy, G. Redkiye zemli s tochki stroeniya atoma (The Rare Earths from the Standpoint of Atomic Structure), Leningrad, Nauchnoye khimiko-tekhnicheskoye izdatel'stvo, 1929.
41. Shvey, I. V. Geologiya mestorozhdeniy redkikh elementov. Osnovnye voprosy geokhimii r. z. e. i ittriya v endogennykh protsessakh (The Geology of Deposits of Rare Elements. The Principal Problems of the Geochemistry of the Rare Earth Elements and Yttrium in Endogenetic Processes), Moscow, Gosudarstvennoye nauchno-tekhnicheskoye izdatel'stvo literatury po geologii i okhrane nedr, No. 15, 1962.
42. Berman, S. Geochim. et Cosmochim. Acta, 12, N 3, 271, 1957.
43. Cameron, A. G. W. Astrophys. J., 129, 1959.
44. Eberhard, G. Berl. Berichte, 1, 851, 1908.
45. Goldschmidt, V. M. and Thomassen, L. Skr. Vidensk. Selsk. Oslo, Mat.-Naturv. Kl. 5, 1924.
46. Goldschmidt, V. M., Ulrich, F. and Barth, T. Skr. Vid. Selsk. Oslo, Mat.-Naturv. Kl. N 5, 1925.
47. Goldschmidt, V. M. Geochem. Vert. der Elemente, VII, 1926.
48. Goldschmidt, V. M. Die Naturwissenschaften, 18, 1930.
49. Goldschmidt, V. M. Handworterbuch der Naturwissenschaften, In 2-te Aufl., Jena, 1933.

50. Goldschmidt, V. M. Chem. Soc., 19, 1937.
51. Goldschmidt, V. M. Geochemistry, Oxford, 1954.
52. Landergren, S. t. Jernkontorets Annaler, 711, 1936.
53. Masuda, A. J. Earth. Sci. Nagoya Univ., 5, 1957.
54. Minami, E. Nachr. Ges. Wiss. Gottingen. Math-phys. Kl (IV), 1, 1935.
55. Murata, K. J., Rose, H. J. and Carron, M. K. Geochim. et Cosmochim. Acta, 4, 1953.
56. Murata, K. J., Rose, H. J., Carron, M. K. and Glass, J. Geochim. et Cosmochim. Acta, 11, N 3, 1957.
57. Noddack, J. Z. anorg. Chem., 225, 1935.
58. Rankama, K. and Sahama, T. G. Geochemistry, Chicago, 1950.
59. Russell, H. N. Astrophys. J., 70, 1929.
60. Sahama, Th. G. and Yahatalo, V. Bull. Comm. geol. Finl., N 126, 1939.
61. Sahama, Th. G. Bull. Comm. geol. Finl., N 136, 1945.
62. Sen, N., Nockolds, S. R. and Allen, R. Geochim. et Cosmochim. Acta, 16, N 1/3, 58, 1959.
63. Schmitt, R. A., Mosen, A. W., Suffredini, C. S., Lasch, L. E., Sharp, R. A. and Oleny, D. A. Nature, 186, N 4728, 1960.
64. Suess, H. E. and Urey, H. C. Rev. Mod. Phys., 28, 1956.
65. Van Tongeren, W. Contributions to the Knowledge of the Chemical Composition of the Earth's Crust in the East Indian Archipelago, Amsterdam, 1938.
66. Taylor, S. R. Geochim. et Cosmochim. Acta, 19, N 2, 1960.
67. Taylor, S. R. Geochim. et Cosmochim. Acta, 26, N 1, 1962.

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